



Formation of a hydrogen plasma from an incandescently heated hydrogen-catalyst gas mixture with an anomalous afterglow duration

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Abstract

We report the generation of a plasma of hydrogen and certain alkali ions as recorded via EUV spectroscopy and the hydrogen Balmer and alkali line emissions in the visible range. Typically, a hydrogen plasma is generated and the emission of extreme ultraviolet light from hydrogen gas is achieved via a discharge at high voltage, a high power inductively coupled plasma, or a plasma created and heated to extreme temperatures by RF coupling (e.g. $> 10^6$ K) with confinement provided by a toroidal magnetic field. The observed plasma formed at low temperatures (e.g. $\approx 10^3$ K) from atomic hydrogen generated at a tungsten filament that heated a titanium dissociator and a catalyst comprising one of potassium, rubidium, cesium, and their carbonates and nitrates. These atoms and ions ionize to provide a catalyst with a net enthalpy of reaction of an integer multiple of the potential energy of atomic hydrogen ($m \times 27.2$ eV $m = \text{integer}$) to within 0.17% and comprise only a single ionization in the case of a potassium or rubidium ion. Whereas, the chemically similar atoms of sodium and lithium and lithium carbonates and nitrates which do not ionize with these constraints caused no emission. To test the electric dependence of the emission, the weak electric field of about 1 V/cm was set and measured to be zero in $< 0.5 \times 10^{-6}$ s. An anomalous afterglow duration of about 1–2 s was recorded in the case of potassium, rubidium, cesium, K_2CO_3 , RbNO_3 , and CsNO_3 . Hydrogen line or alkali line emission was occurring even though the voltage between the heater wires was set to and measured to be zero. These atoms and ions ionize to provide a catalyst with a net enthalpy of reaction of an integer multiple of the potential energy of atomic hydrogen to within less than the thermal energies at $\approx 10^3$ K and comprise only a single ionization in the case of a potassium or rubidium ion. Since the thermal decay time of the filament for dissociation of molecular hydrogen to atomic hydrogen was similar to the anomalous plasma afterglow duration, the emission was determined to be due to a reaction of atomic hydrogen with a catalyst that did not require the presence of an electric field to be functional. © 2001 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

A historical motivation to cause EUV emission from a hydrogen gas was that the spectrum of hydrogen was first recorded from the only known source, the Sun [1]. Developed sources that provide a suitable intensity are high voltage discharge, synchrotron, and inductively coupled plasma generators [2]. An important variant of the later type of source is a tokomak [3]. Fujimoto et al. [4] have deter-

mined the cross section for production of excited hydrogen atoms from the emission cross sections for Lyman and Balmer lines when molecular hydrogen is dissociated into excited atoms by electron collisions. These data were used to develop a collisional-radiative model to be used in determining the ratio of molecular-to-atomic hydrogen densities in tokomak plasmas. Their results indicate an excitation threshold of 17 eV for Lyman α emission. Addition of other gases would be expected to decrease the intensity of hydrogen lines which could be absorbed by the gas. Hollander and Wertheimer [5] found that within a selected range of parameters of a plasma created in a microwave resonator cavity, a hydrogen–oxygen plasma displays an emission that resem-

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bles the absorption of molecular oxygen. Whereas, a helium-hydrogen plasma emits a very intense hydrogen Lyman α radiation at 121.5 nm which is up to 40 times more intense than other lines in the spectrum. The Lyman α emission intensity showed a significant increase from that predicted by the model of Fujimoto et al. [4] and from the emission of hydrogen alone.

Observation of intense extreme ultraviolet (EUV) emission has been previously reported at low temperatures (e.g. $\approx 10^3$ K) from atomic hydrogen and certain atomized elements or certain gaseous ions [6-17]. The only pure elements that were observed to emit EUV were those wherein the ionization of t electrons from an atom to a continuum energy level is such that the sum of the ionization energies of the t electrons is approximately $m \times 27.2$ eV where t and m are each an integer. Potassium, cesium, and strontium atoms and Rb^+ ion ionize at integer multiples of the potential energy of atomic hydrogen and caused emission. Whereas, the chemically similar atoms, sodium, magnesium and barium, do not ionize at integer multiples of the potential energy of atomic hydrogen and caused no emission. Helium ions present in the experiment of Hollander and Wertheimer [5] ionize at a multiple of 2 times the potential energy of atomic hydrogen.

Prior studies support the possibility of a novel reaction of atomic hydrogen which produces an anomalous discharge and produces novel hydride compounds [6-31]. Experiments that confirm the novel hydrogen chemistry include extreme ultraviolet (EUV) spectroscopy, plasma formation, power generation, and analysis of chemical compounds. For examples: (1) Lines observed by EUV spectroscopy could be assigned to transitions of atomic hydrogen to lower energy levels corresponding to lower energy hydrogen atoms and the emission from the excitation of the corresponding hydride ions [8,11,13,15-17]. (2) The chemical interaction of catalysts with atomic hydrogen at temperatures below 1000 K has shown surprising results in terms of the emission of the Lyman and Balmer lines [6-17] and the formation of novel chemical compounds [13,15-31]. (3) An energetic plasma in hydrogen was generated by a catalytic reaction at 1% of the theoretical or prior known voltage requirement and with 1000s of times less power input in a system wherein the plasma reaction was controlled with a weak electric field [6,10]. (4) An anomalous plasma with hydrogen/potassium mixtures has been reported where the plasma decayed with a two second half-life which was the thermal decay time of the filament which dissociated molecular hydrogen to atomic hydrogen when the electric field was set to zero [9]. This experiment showed that hydrogen line emission was occurring even though the voltage between the heater wires was set to 0 and measured to be zero and indicated that the emission was due to a reaction of potassium atoms with atomic hydrogen. (5) Novel hydrogen compounds have been isolated as products of the reaction of atomic hydrogen with atoms and ions identified as catalysts in the reported EUV studies [6-31].

We report that a hydrogen plasma formed at low temperatures (e.g. $\approx 10^3$ K) by reaction of atomic hydrogen with a catalyst with a net enthalpy of reaction of an integer multiple of the potential energy of atomic hydrogen ($m \times 27.2$ eV $m = \text{integer}$). Atomic hydrogen was generated by dissociation at a tungsten filament and at a transition metal dissociator that was incandescently heated by the filament. Catalyst atoms or ions were vaporized by heating to form a low vapor pressure (e.g. 1 Torr). The kinetic energy of the thermal electrons at the experimental temperature of $\approx 10^3$ K were about 0.1-0.2 eV, and the average collisional energies of electrons accelerated by the field of the filament were less than 1 eV. (No blackbody emission was recorded for wavelengths shorter than 400 nm.) Only blackbody radiation was observed at lower wavelengths unless an anomalous discharge formed. The mechanism of EUV emission cannot be explained by the conventional chemistry of hydrogen, but it is predicted by a solution of the Schrodinger equation with a nonradiative boundary constraint put forward by Mills [32].

Mills predicts that certain atoms or ions serve as catalysts to release energy from hydrogen to produce an increased binding energy hydrogen atom called a *hydrino atom* having a binding energy of

$$\text{Binding energy} = \frac{13.6}{n^2}, \quad (1)$$

where

$$n = \frac{1}{2}, \frac{1}{3}, \dots, p \quad (2)$$

and p is an integer greater than 1, designated as $\text{H}[a_{\text{H}}/p]$ where a_{H} is the radius of the hydrogen atom. Hydrinos are predicted to form by reacting an ordinary hydrogen atom with a catalyst having a net enthalpy of reaction of about

$$m \times 27.2 \text{ eV}, \quad (3)$$

where m is an integer. This catalysis releases energy from the hydrogen atom with a commensurate decrease in size of the hydrogen atom, $r_n = n a_{\text{H}}$. For example, the catalysis of $\text{H}(n = 1)$ to $\text{H}(n = 1/2)$ releases 40.8 eV, and the hydrogen radius decreases from a_{H} to $\frac{1}{2}a_{\text{H}}$.

The excited energy states of atomic hydrogen are also given by Eq. (1) except that

$$n = 1, 2, 3, \dots \quad (4)$$

The $n = 1$ state is the "ground" state for "pure" photon transitions (the $n = 1$ state can absorb a photon and go to an excited electronic state, but it cannot release a photon and go to a lower-energy electronic state). However, an electron transition from the ground state to a lower-energy state is possible by a nonradiative energy transfer such as multipole coupling or a resonant collision mechanism. These lower-energy states have fractional quantum numbers, $n = 1/\text{integer}$. Processes that occur without photons and that require collisions are common. For example, the exothermic chemical reaction of $\text{H} + \text{H}$ to form H_2 does not

occur with the emission of a photon. Rather, the reaction requires a collision with a third body, M, to remove the bond energy $H + H + M \rightarrow H_2 + M^*$ [33]. The third body distributes the energy from the exothermic reaction, and the end result is the H_2 molecule and an increase in the temperature of the system. Some commercial phosphors are based on nonradiative energy transfer involving multipole coupling. For example, the strong absorption strength of Sb^{3+} ions along with the efficient nonradiative transfer of excitation from Sb^{3+} to Mn^{2+} , are responsible for the strong manganese luminescence from phosphors containing these ions [34]. Similarly, the $n = 1$ state of hydrogen and the $n = 1/integer$ states of hydrogen are nonradiative, but a transition between two nonradiative states is possible via a nonradiative energy transfer, say $n = 1-1/2$. In these cases, during the transition the electron couples to another electron transition, electron transfer reaction, or inelastic scattering reaction which can absorb the exact amount of energy that must be removed from the hydrogen atom. Thus, a catalyst provides a net positive enthalpy of reaction of $m \times 27.2$ eV (i.e. it absorbs $m \times 27.2$ eV where m is an integer). Certain atoms or ions serve as catalysts which resonantly accept energy from hydrogen atoms and release the energy to the surroundings to effect electronic transitions to fractional quantum energy levels. Recent analysis of mobility and spectroscopy data of individual electrons in liquid helium show direct experimental evidence that electrons may have fractional principal quantum energy levels [35].

The catalysis of hydrogen involves the nonradiative transfer of energy from atomic hydrogen to a catalyst which may then release the transferred energy by radiative and nonradiative mechanisms. As a consequence of the nonradiative energy transfer, the hydrogen atom becomes unstable and emits further energy until it achieves a lower-energy nonradiative state having a principal energy level given by Eqs. (1) and (2).

The energy released during catalysis may undergo internal conversion and cause alkali line emission. The energy could also ionize or excite molecular and atomic hydrogen resulting in hydrogen emission which includes well characterized ultraviolet lines such as the Lyman series and the visible Balmer series. The existence of Balmer emission requires that Lyman emission is also generated. This confirms that a hydrogen plasma exists. Lyman α emission was sought by EUV spectroscopy, and Balmer and alkali line emission was sought by visible spectroscopy.

The temporal behavior of the light emission in the visible range was recorded when all of the power into the cell was removed. Typically, the temporal emission of a plasma is very short. For example, the afterglow with decay to zero emission of cesium lines (e.g. 455.5 nm) of a high voltage pulse discharge is about 100 μ s [36]. And, the duration of the afterglow of a neon plasma which was switched off from a stationary state was under 250 μ s [37]. In the present study, the presence of EUV emission and the persistence of Balmer beta or alkali line emission when the field was zero

was a means to determine whether the plasma was due to the externally applied power or whether a novel chemical source of power that required a catalyst and hydrogen was responsible. The electric field dependence of the catalysts was also determined.

2. Experimental

Due to the extremely short wavelength of this radiation, "transparent" optics do not exist. Therefore, a windowless arrangement was used wherein the source was connected to the same vacuum vessel as the grating and detectors of the EUV spectrometer. Windowless EUV spectroscopy was performed with an extreme ultraviolet spectrometer that was mated with the cell. Differential pumping permitted a high pressure in the cell as compared to that in the spectrometer. This was achieved by pumping on the cell outlet and pumping on the grating side of the collimator that served as a pin-hole inlet to the optics. The cell was operated under hydrogen flow conditions while maintaining a constant hydrogen pressure in the cell with a mass flow controller.

The experimental set up shown in Fig. 1 comprised a quartz cell which was 510 mm in length and 50 mm in diameter. Three ports for grating, outlet, and photon detection were on the other end of the cell. A tungsten filament (0.508 mm in diameter and 800 cm in length, total resistance $\sim 2.5\ \Omega$) and a titanium cylindrical screen (300 mm long and 40 mm in diameter) that performed as a hydrogen dissociator were inside the quartz cell. A new dissociator was used for each experiment. The filament was coiled on a grooved ceramic support to maintain its shape when heated. The return lead ran through the middle of the ceramic support. The filament leads were covered by a alumina sheath which differed from the set up reported previously [7]. The titanium screen was electrically floated. The power was applied to the filament by a power supply (Sorensen 80-13) which was controlled by a constant power controller. The cell was operated with 300 W or less input power which corresponded to a cell wall temperature of about 700 $^{\circ}$ C or less which was lower than the maximum power and temperature, respectively, reported in previous EUV studies [7]. This temperature was selected in order to maximize the vaporization of the catalyst while avoiding decomposition to the corresponding alkali metal in the case of alkali carbonates and nitrates. The temperature of the tungsten filament was estimated to be in the range of 1100–1500 $^{\circ}$ C. The hydrogen gas pressure inside the cell was maintained at about 300 mTorr. The entire quartz cell was enclosed inside an insulation package (Zircar AL-30). Several K-type thermocouples were placed in the insulation to measure key temperatures of the cell and insulation. The thermocouples were read with a multichannel computer data acquisition system.

In the present study, the light emission phenomena was studied for (1) hydrogen, argon, neon, and helium alone, (2) all alkali metals except lithium which reacted with the quartz cell and all alkali carbonates

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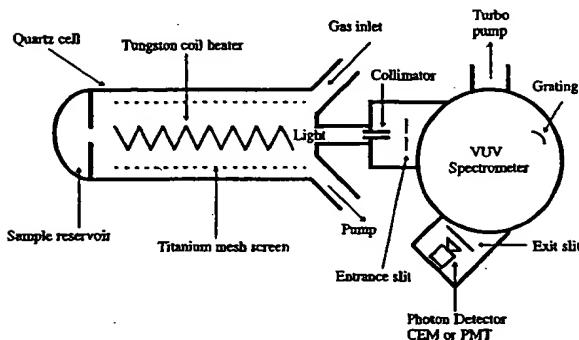


Fig. 1. The experimental set up comprising a gas cell light source and an EUV spectrometer which was differentially pumped.

and nitrates. The inorganic test materials were coated on a titanium screen dissociator by the method of wet impregnation. The screen was coated by dipping it in a 0.6 M Na_2CO_3 /10% H_2O_2 , 0.6 M K_2CO_3 /10% H_2O_2 , or 0.6 M RbNO_3 /10% H_2O_2 solution, and the crystalline material was dried on the surface by heating for 12 h in a drying oven at 130°C. A new dissociator was used for each experiment. Alkali metals were placed in the bottom of the cell and volatilized by the external heater.

The light emission was introduced to an EUV spectrometer for spectral measurement. The spectrometer was a McPherson 0.2 m monochromator (Model 302, Seya-Namioka type) equipped with a 1200 lines/mm holographic grating with a platinum coating. The wavelength region covered by the monochromator was 30–560 nm. The vacuum inside the monochromator was maintained below 5×10^{-4} Torr by a turbo pump.

The EUV spectrum (40–160 nm) of the cell emission was recorded with a channel electron multiplier (CEM). The wavelength resolution was about 1 nm (FWHM) with an entrance and exit slit width of $300 \times 300 \mu\text{m}$ except for the Na_2CO_3 cell wherein an entrance and exit slit width of $500 \times 500 \mu\text{m}$ was used.

The EUV/UV/VIS spectrum (40–560 nm) of the cell emission of hydrogen alone was recorded with a photomultiplier tube (PMT) and a sodium salicylate scintillator. The PMT (Model R1527P, Hamamatsu) used has a spectral response in the range of 185–560 nm with a peak efficiency at about 400 nm. The scan interval was 0.4 nm. The inlet and outlet slit were $500 \times 500 \mu\text{m}$ which corresponded to a wavelength resolution of about 2 nm (FWHM).

The UV/VIS spectrum (400–560 nm) of the cell emission was recorded with the photomultiplier tube (PMT) without the sodium salicylate scintillator. The scan interval was 0.4 nm. The inlet and outlet slit were $500 \times 500 \mu\text{m}$.

The emission in the region 560–900 nm was recorded with a 100 μm optical fiber and visible spectrometer (Ocean Optics S2000). To correct for the nonuniform response of the spectrometer system as a function of wavelength and the dependence of energy on wavelength, the system was calibrated against a reference light source (Ocean Optics

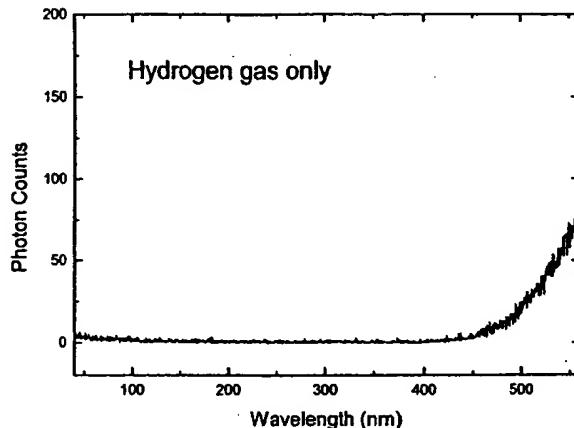


Fig. 2. The UV/VIS spectrum (40–560 nm) of the cell emission from the gas cell comprising a tungsten filament, a titanium dissociator, and 0.3 Torr hydrogen at a cell temperature of 700°C that was recorded with a PMT and a sodium salicylate scintillator with an increased slit width of $500 \times 500 \mu\text{m}$.

LS-1-CAL). A spectral calibration factor was applied to the count rate data at each wavelength to yield the irradiation of the detector in units of energy/time/area/wavelength.

In order to study the temporal behavior of the cell, UV/VIS spectrometer was set to the Balmer beta line or a alkali line and the current of the heater was interrupted by a switch between the power supply and the filament. This switch set the voltage to zero in $< 0.5 \times 10^{-6}$ s as recorded by an oscilloscope (BK Precision Model 2120). The response time of the photomultiplier was also tested by switching off the room lights and recording the zero order as a function of time. The emission in the 300–560 nm region was recorded as a function of time at 200 ms steps with the photomultiplier as the filament was switched on and off. The emission in the 560–900 nm region was recorded as a function of time at 200 ms steps with the Ocean Optics S2000 spectrometer as the filament was switched on and off.

3. Results

The cell without any test material present was run to establish the baseline of the spectrometer. The UV/VIS spectrum (40–560 nm) of the emission from the gas cell comprising a tungsten filament, a titanium dissociator, and 0.3 Torr hydrogen at a cell temperature of 700°C is shown in Fig. 2. No emission was observed except for the blackbody filament radiation at the longer wavelengths. No emission was also observed when argon, neon, or helium replaced hydrogen.

The EUV spectrum (40–160 nm) of the cell emission from the Na_2CO_3 , K_2CO_3 , and RbNO_3 gas cell is shown in Figs. 3–5, respectively. Even with the larger slit widths, essentially no EUV emission was observed in the case of Na_2CO_3 which is not a catalyst. The cause of the weak emission may have been due to potassium contamination

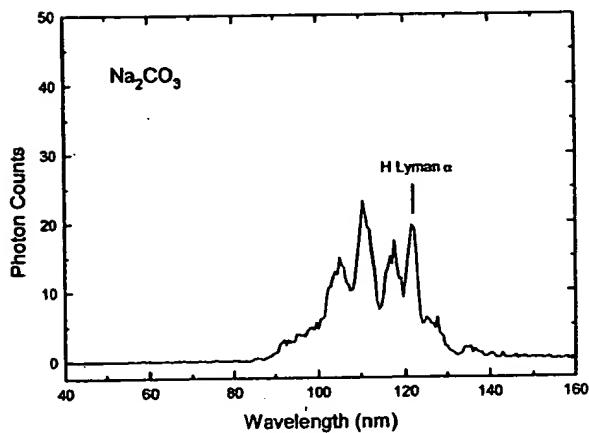


Fig. 3. The EUV spectrum (40–160 nm) of the cell emission from the gas cell comprising a tungsten filament, a titanium dissociator treated with 0.6 M Na_2CO_3 /10% H_2O_2 before being used in the cell, and 0.3 Torr hydrogen at a cell temperature of 700 °C that was recorded with a CEM with an increased slit width of $500 \times 500 \mu\text{m}$.

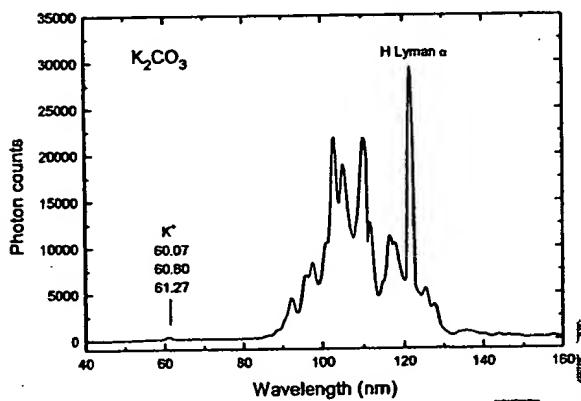


Fig. 4. The EUV spectrum (40–160 nm) of the cell emission from the gas cell comprising a tungsten filament, a titanium dissociator treated with 0.6 M K_2CO_3 /10% H_2O_2 before being used in the cell, and 0.3 Torr hydrogen at a cell temperature of 700 °C that was recorded with a CEM.

which was observed by time of flight secondary ion mass spectroscopy. Strong emission of hydrogen Lyman series and weak potassium and rubidium lines were observed in the cases of catalysts K_2CO_3 and RbNO_3 , respectively. In these cases, the EUV emission indicated that a plasma of hydrogen and alkali ion was present with emissions 10 times more energetic than known chemical reactions.

The UV/VIS spectrum (300–560 nm) of the cell emission from the Na_2CO_3 , K_2CO_3 , and RbNO_3 gas cell is shown in Figs. 6–8, respectively. No UV/VIS emission was observed in the case of Na_2CO_3 which is not a catalyst; whereas, strong emission was observed in the cases of catalysts K_2CO_3 and RbNO_3 . In the case of K_2CO_3 , the visible spectrum shown in Fig. 7 contains potassium lines

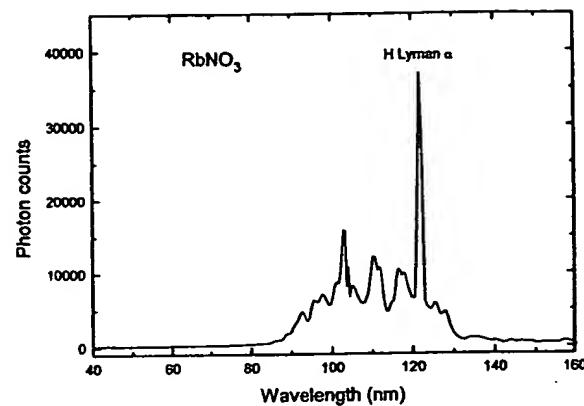


Fig. 5. The EUV spectrum (40–160 nm) of the cell emission from the gas cell comprising a tungsten filament, a titanium dissociator treated with 0.6 M RbNO_3 /10% H_2O_2 before being used in the cell, and 0.3 Torr hydrogen at a cell temperature of 700 °C that was recorded with a CEM.

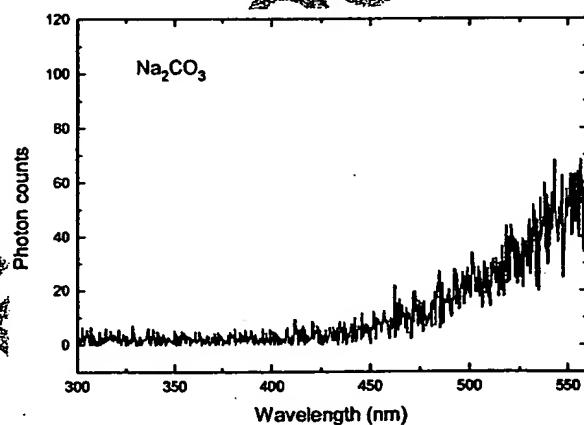


Fig. 6. The UV/VIS spectrum (300–560 nm) of the cell emission from the gas cell comprising a tungsten filament, a titanium dissociator treated with 0.6 M Na_2CO_3 /10% H_2O_2 before being used in the cell, and 0.3 Torr hydrogen at a cell temperature of 700 °C that was recorded with a PMT.

and hydrogen Balmer lines. Balmer beta was present at 486 nm, and Balmer gamma was present at 434 nm when the Lyman α emission was present in the EUV region. Thus, recording the Balmer emission corresponds to recording the Lyman α emission. The Balmer beta was selected and the temporal behavior of the light emission in the visible range was recorded when all of the power into the cell was removed. In the case of RbNO_3 , the visible spectrum shown in Fig. 8 contains rubidium lines. The rubidium 550.0 nm was present when the Lyman α emission was present in the EUV region. Thus, recording the rubidium 550.0 nm corresponds to recording the Lyman α emission. The rubidium 550.0 nm was selected and the temporal behavior of the light emission

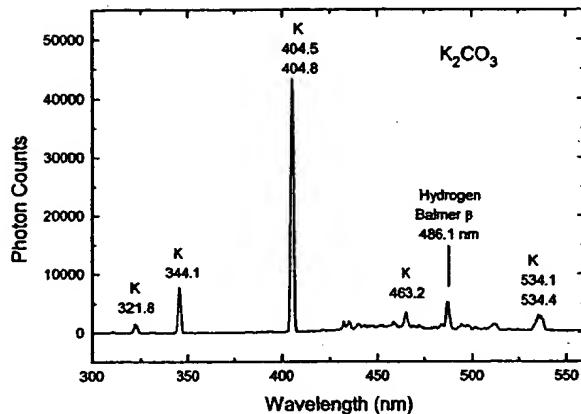


Fig. 7. The UV/VIS spectrum (300–560 nm) of the cell emission from the gas cell comprising a tungsten filament, a titanium dissociator treated with 0.6 M K_2CO_3 /10% H_2O_2 before being used in the cell, and 0.3 Torr hydrogen at a cell temperature of 700°C that was recorded with a PMT.

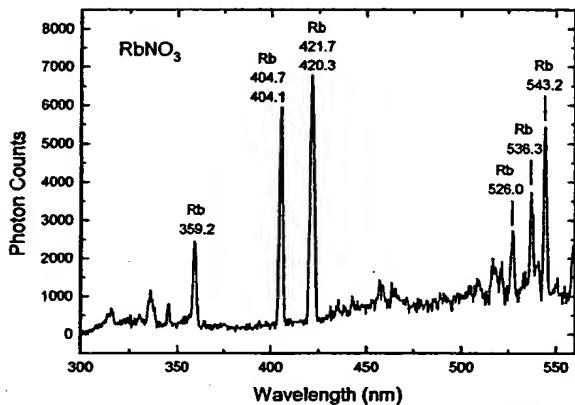


Fig. 8. The UV/VIS spectrum (300–560 nm) of the cell emission from the gas cell comprising a tungsten filament, a titanium dissociator treated with 0.6 M RbNO_3 /10% H_2O_2 before being used in the cell, and 0.3 Torr hydrogen at a cell temperature of 700°C that was recorded with a PMT.

in the visible range was recorded when all of the power into the cell was removed.

The temporal behavior of the filament was studied following the interruption and restoration of the power. The monochromator was adjusted to the range around 670 nm, a part of the spectrum where no line radiation was observed, and the blackbody radiation from the heater was significant. It took about 10 min before the blackbody of the filament reached a steady level. Then, the heater current was interrupted several times. The thermal decay time of the filament for dissociation of molecular hydrogen to atomic hydrogen was about 2 s.

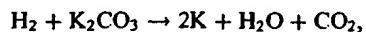
Next, the temporal behavior of the plasma was studied following the interruption of the heater power. Only the cell containing a catalyst comprising one of potassium, rubid-

ium, cesium, and their carbonates and nitrates with hydrogen was studied since these were the only cases in which a plasma was formed. A bright plasma formed by the time the cell temperature reached 700°C. A spectrum was obtained over the region 300–560 nm. The visible lines of maximum intensity were identified and the monochromator was adjusted to the observed lines. For example, in the case of K_2CO_3 and RbNO_3 , the monochromator was adjusted to the Balmer beta line at 486 nm, and the rubidium 550.0 nm emission, respectively. In both cases, the line appeared as a part of the spectrum where the blackbody radiation from the heater was essentially zero as shown in Figs. 2, 7 and 8, respectively. The response time of the photomultiplier was tested by switching off the room lights and recording the zero order as a function of time. The results are shown in Fig. 9. The photomultiplier output went to zero within the sampling time (200 ms) of the photomultiplier. With a faster rate, this time constant may be reduced. The heater current was interrupted several times with sufficient spacing between the interruptions, so that the line emission always returned to its previous level. The switch set the voltage to zero in a $< 0.5 \times 10^{-6}$ s as recorded by the oscilloscope (BK Precision Model 2420), and the output of the photomultiplier was recorded. In the case of K_2CO_3 and RbNO_3 , the emission of the cell as a function of time while the heater power was turned on and off is shown in Figs. 10(a)–(c) and 11, respectively. The observed decay time of the emission was about 1–2 s.

The atoms and ions which gave an anomalous discharge as determined by strong EUV and visible emission are given in Table 1. The atoms and ions which gave an anomalous afterglow duration of about 1–2 s are also given in Table 1 with the corresponding line emission(s).

4. Discussion

Only blackbody radiation was observed at lower wavelengths unless an anomalous discharge formed. In the cases where plasma was observed, no possible chemical reactions of the tungsten filament, the titanium dissociator, catalyst, and 0.3 Torr hydrogen at a cell temperature of 700°C could be found which accounted for the plasma. In fact, no known chemical reaction releases enough energy to form a hydrogen plasma. For examples, the enthalpy of formation ΔH_f of potassium, rubidium, and cesium hydride is -14.13 , -13.00 , and -13.50 kcal/mol [38]. Thus, the formation of potassium, rubidium, and cesium hydride releases 0.59 , 0.54 , and 0.56 eV/atom, respectively. The reduction of K_2CO_3 by hydrogen calculated from the heats of formation is very endothermic.



$$\Delta H = +122.08 \text{ kcal/mol H}_2. \quad (5)$$

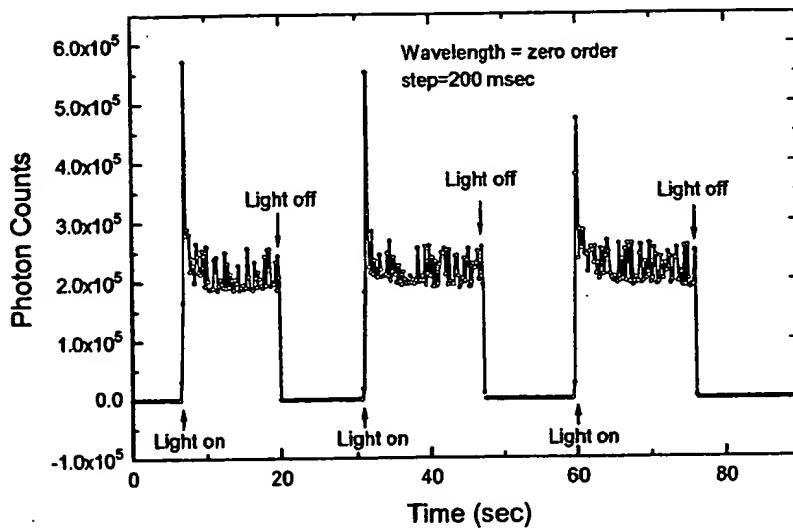
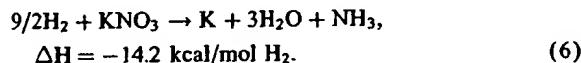


Fig. 9. The response time of the photomultiplier tested by switching off the room lights and recording the zero order as a function of time.

The reaction absorbs 2.5 eV/hydrogen atom. The reduction of KNO_3 to water, potassium metal, and NH_3 calculated from the heats of formation only releases 0.3 eV/hydrogen atom.



The most energetic reaction possible was the reaction of hydrogen to form water which releases 1.48 eV per atom of hydrogen; whereas, the energy of Lyman emission is greater than 10.2 eV/atom.

The dissociator was present in all experiments. The emission was not observed with the cell alone, with hydrogen, helium, neon, or argon alone, or under identical conditions wherein a noncatalyst replaced a catalyst. When the power was interrupted, the emission decayed in about 2 s. Decay was recorded over a time greater than 0.099 times the typical duration of a discharge plasma afterglow [36]. This experiment shows, that plasma emission was occurring even though the voltage between the heater wires was set to and measured to be zero for a time duration which was anomalous. Since the thermal decay time of the filament for dissociation of molecular hydrogen to atomic hydrogen was similar to the anomalous plasma afterglow duration which required the presence of a catalyst, the emission was determined to be due to a reaction of catalyst with atomic hydrogen.

In the present study, the filament leads were covered by a alumina sheath which differed from the set up reported previously [7]. It was found in previous studies that a weak electric field was required in order for a resonance energy match to be achieved between an atom of hydrogen and a catalyst atom or ion such as a strontium atom [6,10]. A further goal of the present study was to determine the field

dependence of EUV emission and to demonstrate an anomalous afterglow with no field present. In previous studies [7] the maximum field was about 10 V/cm between the leads with a dipole field along the length of the filament of about 1 V/cm. In the present cell only the weak dipole field of 1 V/cm was present until the power to the filament was switched off. In either case, the field was negligible relative to that which causes an electrical discharge. At the same hydrogen pressure as that of the present studies, breakdown did not occur for an applied voltage of less than 3000 V or about 1000 V/cm across the leads with the filament disconnected. In this case, only an arc formed versus a plasma which filled the entire cell when a catalyst and atomic hydrogen from the filament were present. With the field minimized, only those catalysts with a net enthalpy of reaction of an integer multiple of the potential energy of atomic hydrogen ($m \times 27.2 \text{ eV}$ $m = \text{integer}$) to within 0.17 eV and involve only a single ionization form in the case of a catalyst ion produced EUV and visible emission as shown in Table 1. And, only those catalysts with a net enthalpy of reaction of an integer multiple of the potential energy of atomic hydrogen to within less than the thermal energies at $\approx 10^3 \text{ K}$ and involve only a single ionization in the case of a catalyst ion produced an anomalous plasma afterglow duration as shown in Table 1.

4.1. Catalysts

The emission must have been due to a novel chemical reaction between catalyst and atomic hydrogen. According to Mills [32], a catalytic system is provided by the ionization of t electrons from an atom or ion to a continuum energy level such that the sum of the ionization energies of the t electrons is approximately $m \times 27.2 \text{ eV}$ where m is an

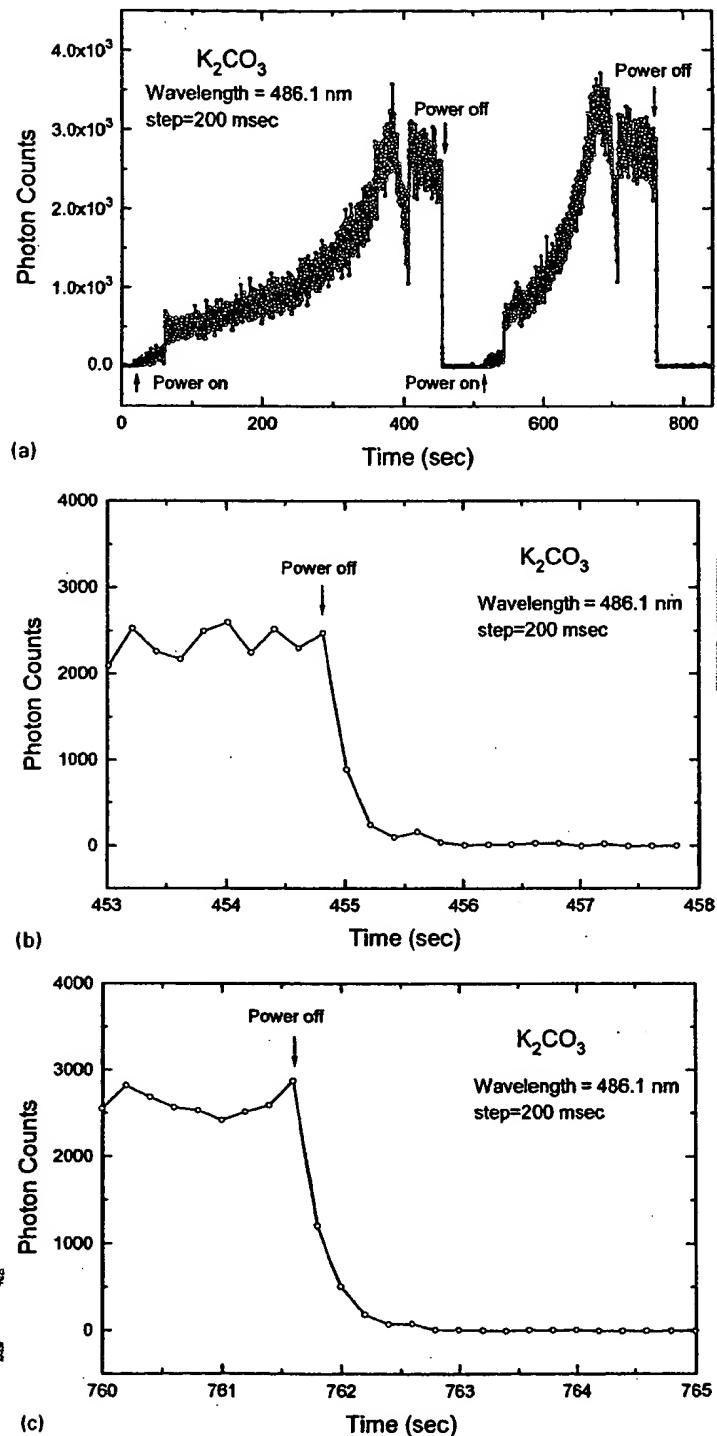


Fig. 10. (a) The emission of the 486.1 nm hydrogen Balmer β line as a function of time while the heater power was turned on and off. The gas cell comprised a tungsten filament, a titanium dissociator treated with 0.6 M K₂CO₃/10% H₂O₂ before being used in the cell, and 0.5 torr hydrogen at a cell temperature of 700°C that was recorded at 200 ms intervals with a PMT. (b) The expanded region 453–458 s shown in Fig. 10(a) of the emission of the 486.1 nm hydrogen Balmer β line as a function of time showing the decay when the heater power was turned off. (c) The expanded region 760–765 s shown in Fig. 10(a) of the emission of the 486.1 nm hydrogen Balmer β line as a function of time showing the decay when the heater power was turned off.

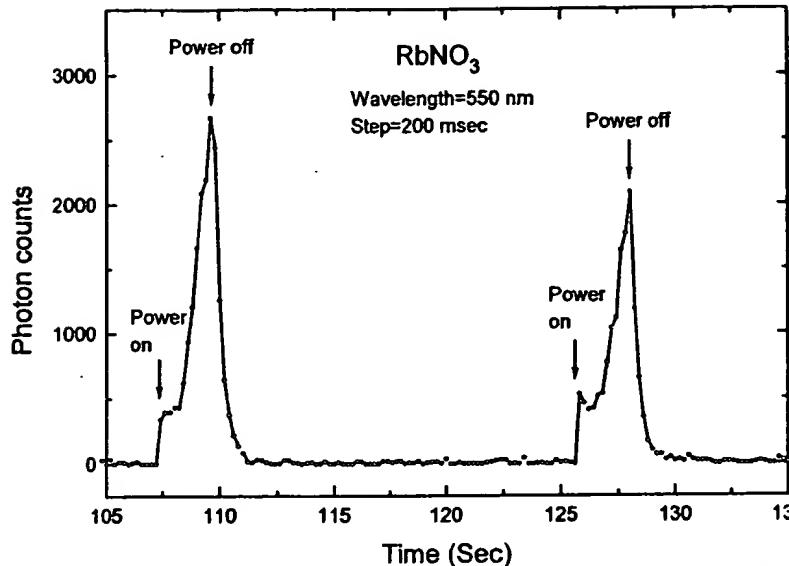
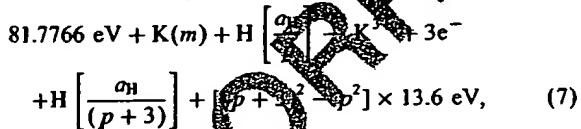


Fig. 11. The emission of the Rb 550.0 nm line as a function of time while the heater power was turned on and off. The gas cell comprised a tungsten filament, a titanium dissociator treated with 0.6 M RbNO₃/10% H₂O₂ before being used in the cell, and 0.3 Torr hydrogen at a cell temperature of 700°C that was recorded at 200 ms intervals with a PMT.

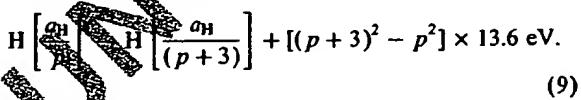
integer. A catalyst may also be provided by the transfer of t electrons between participating ions. The transfer of t electrons from one ion to another ion provides a net enthalpy of reaction whereby the sum of the ionization energy of the electron donating ion minus the ionization energy of the electron accepting ion equals approximately $m \times 27.2$ eV where t and m are each an integer.

4.2. Potassium metal

One such atomic catalytic system involves potassium metal. The first, second, and third ionization energies of potassium are 4.34066, 31.63, 45.806 eV, respectively [39]. The triple ionization ($t = 3$) reaction of K to K³⁺, then, has a net enthalpy of reaction of 81.7766 eV, which is equivalent to $m = 3$ in Eq. (3).



The overall reaction is



The anomalous afterglow of potassium metal may be possible since the triple ionization ($t = 3$) reaction of K-K²⁺ has a net enthalpy of reaction of 81.7766 eV, which is within

thermal energies of 3×27.2 eV. And, the potassium atom is neutral so that a counter-ion would not effect the vacuum ionization energies.

Also, the anomalous afterglow of potassium metal may be due to catalysis by potassium ions which provide an net enthalpy of reaction of 27.28 eV which is essentially resonance with the 27.2 eV from atomic hydrogen. Strong K⁺ emission was observed in the EUV spectrum.

Also, the identification of the predicted product of catalysis by potassium ions as well as by potassium metal [18] when only potassium metal was supplied as the catalyst provides support for the catalyst by potassium ions as the basis of the anomalous afterglow when potassium metal is supplied.

4.3. Potassium carbonate and potassium nitrate

Potassium ions can also provide a net enthalpy of a multiple of that of the potential energy of the hydrogen atom. The second ionization energy of potassium is 31.63 eV; and K⁺ releases 4.34 eV when it is reduced to K. The combination of reactions K⁺ to K²⁺ and K⁺ to K, then, has a net enthalpy of reaction of 27.28 eV, which is equivalent to $m = 1$ in Eq. (3).

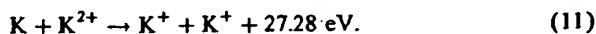
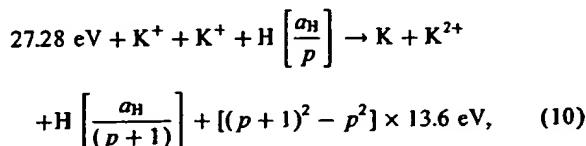
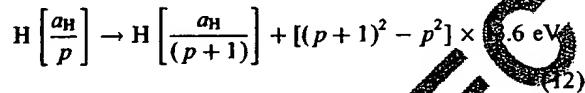


Table 1

Observation of EUV and visible emission and anomalous afterglow duration recorded on a hydrogen or alkali line from an incandescently heated gas mixture of hydrogen and an alkali metal, alkali carbonate, or alkali nitrate

Sample	EUV emission	Visible emission	Anomalous afterglow Lines (nm)
Li_2CO_3	No	No	No
LiNO_3	No	No	No
Na(m)	No	No	No
Na_2CO_3	No	No	No
NaNO_3	No	No	No
K(m)	Yes	Yes	Yes K line 536.1
K_2CO_3	Yes	Yes	Yes Balmer β 486.1
KNO_3	Yes	Yes	No
Rb(m)	Yes	Yes	Yes Rb lines 421.6 544.8
Rb_2CO_3	Yes	Yes	No
RbNO_3	Yes	Yes	Yes Rb line 550.0
Cs(m)	Yes	Yes	Yes Cs line 456.3
Cs_2CO_3	Yes	Yes	No
CsNO_3	Yes	Yes	Yes Cs lines 672.0 852.0

The overall reaction is

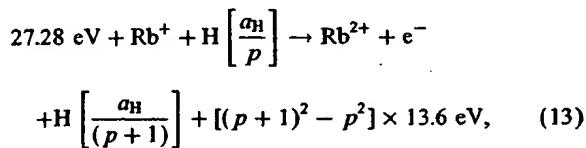


An anomalous afterglow duration was observed for K_2CO_3 but not KNO_3 which indicates that the catalysis reaction given by Eqs. (10)–(12) is favored with K_2CO_3 which provides two potassium ions in the same chemical environment. The EUV spectrum (40–160 nm) of the cell emission for K_2CO_3 is shown in Fig. 4. In addition to K(m) , K_2CO_3 , and KNO_3 , K_2CO_3 produced the highest intensity EUV emission, and the anomalous afterglow duration of the Balmer β line which identified a plasma of hydrogen was present when the electric field was zero shown in Figs. 10(A)–(C) was readily observable.

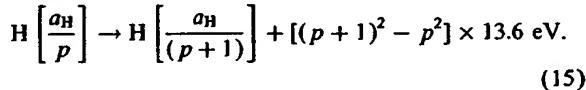
4.4. Rubidium metal, rubidium carbonate, and rubidium nitrate

Rubidium ions can also provide a net enthalpy of a multiple of that of the potential energy of the hydrogen atom. The

second ionization energy of rubidium is 27.28 eV. The reaction Rb^+ to Rb^{2+} has a net enthalpy of reaction of 27.28 eV, which is equivalent to $m = 1$ in Eq. (3).



The overall reaction is



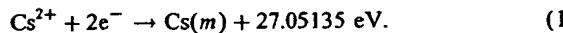
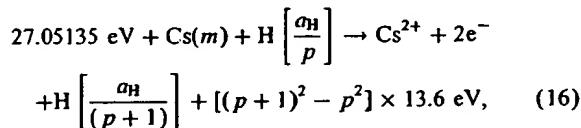
The catalytic rate and corresponding intensity of EUV emission as well as the anomalous afterglow duration probably depends on the concentration of gas phase Rb^+ ions. Rubidium metal may form RbH which may provide gas phase Rb^+ ions, or rubidium metal may be ionized to provide gas phase Rb^+ ions. EUV emission was observed from Rb_2CO_3

which may function as a catalyst. But, an anomalous afterglow duration was not observed possibly because two rubidium ions are present rather than one, and Rb_2CO_3 has a low volatility. In his case, gaseous rubidium from decomposition may be the main source. Rb^+ ion emission was observed in the visible spectrum of rubidium metal and Rb_2CO_3 .

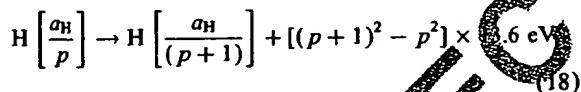
Alkali metal nitrates are extraordinarily volatile and can be distilled at 350–500°C [40]. RbNO_3 is the favored candidate for providing gaseous Rb^+ ions. The EUV spectrum (40–160 nm) of the cell emission for RbNO_3 is shown in Fig. 5. Relative to $\text{Rb}(m)$, Rb_2CO_3 , and RbNO_3 , RbNO_3 produced the highest intensity EUV emission, and the anomalous afterglow duration shown in Fig. 11 was readily observable.

4.5. Cesium metal, cesium carbonate, and cesium nitrate

A catalytic system is provided by the ionization of two electrons from a cesium atom each to a continuum energy level such that the sum of the ionization energies of the two electrons is approximately 27.2 eV. The first and second ionization energies of cesium are 3.89390 and 23.15745 eV, respectively [39]. The double ionization reaction of Cs to Cs^{2+} , then, has a net enthalpy of reaction of 27.05135 eV, which is equivalent to $m = 1$ in Eq. (3).



The overall reaction is

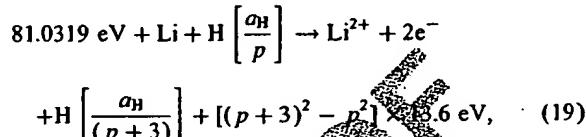


The anomalous afterglow of cesium metal may be possible since the double ionization reaction of $\text{Cs}(m)$ to Cs^{2+} has a net enthalpy of reaction of 27.05135 eV, which is within thermal energies of 2×27.2 eV. And, the cesium atom is neutral so that a counter-ion would not effect the vacuum ionization energies.

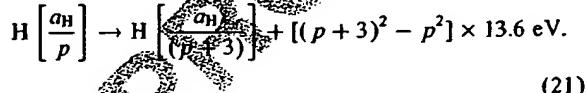
EUV emission was also observed for Cs_2CO_3 , and CsNO_3 . Cs_2CO_3 and CsNO_3 are not catalysts, but they may readily decompose to cesium metal under atomic hydrogen at the cell operating temperature. An anomalous afterglow duration was also observed in the case of CsNO_3 , but not in the case of Cs_2CO_3 . The anomalous afterglow duration of the CsNO_3 gas cell was observed only at long wavelengths indicating that a weak anomalous plasma was present after the heater was turned off. This is consistent with the greater rate of CsNO_3 decomposition relative to Cs_2CO_3 . Strong cesium atom emission was observed in the visible spectrum.

4.6. Lithium metal, lithium carbonate, and lithium nitrate

No EUV emission was observed in the case of LiNO_3 , and Li_2CO_3 which do not provide a reaction with a net enthalpy of a multiple of the potential energy of atomic hydrogen. $\text{Li}(m)$ may function as a catalyst. The catalytic system is provided by the ionization of two electrons from Li to a continuum energy level such that the sum of the ionization energies of the two electrons is approximately 3×27.2 eV. The first and second ionization energies of lithium are 5.39172 eV and 75.64018 eV, respectively [39]. The double ionization reaction of Li to Li^{2+} , then, has a net enthalpy of reaction of 81.0319 eV, which is equivalent to $m = 3$ in Eq. (3).



The overall reaction is

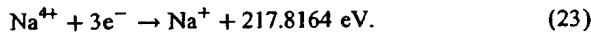
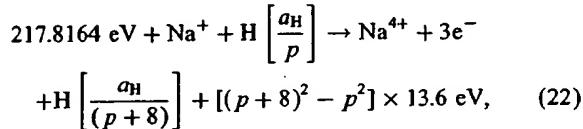


Li_2CO_3 and LiNO_3 are not catalysts, but they may decompose to lithium metal under atomic hydrogen at high temperature. Weak emission was observed previously with the decomposition of Li_2CO_3 and LiNO_3 to lithium metal [7]. Lithium metal did not form to a significant extent in the present study which may explain the absence of emission. Also, the presence of a field of about 10 V/cm may be required in order for a plasma to form in these cases since the mismatch between 81.0319 and 3×27.2 eV is 0.57 eV. In the case that electrons are ionized to a continuum energy level, the presence of a low strength electric field alters the continuum energy levels. In the anomalous discharge of hydrogen due to the presence of lithium, the weak field may adjust the energy of ionizing lithium to match the energy of 3×27.2 eV to permit a novel reaction of atomic hydrogen.

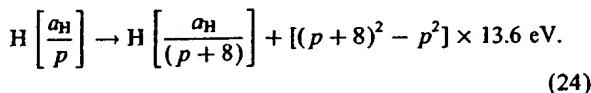
4.7. Sodium metal, sodium carbonate, and sodium nitrate

No EUV emission was observed in the case of $\text{Na}(m)$ which does not provide a reaction with a net enthalpy of a multiple of the potential energy of atomic hydrogen. Na^+ may serve as a catalyst. The catalytic system is provided by the ionization of three electrons from Na^+ to a continuum energy level such that the sum of the ionization energies of the three electrons is approximately 8×27.2 eV. The second, third, and fourth ionization energies of sodium are 47.2864, 71.6200, and 98.91 eV, respectively [39]. The triple ionization reaction of Na^+ to Na^{4+} , then, has a net

enthalpy of reaction of 217.8164 eV, which is equivalent to $m = 8$ in Eq. (3).



The overall reaction is



No emission was observed from Na_2CO_3 which may not function as a catalyst because two sodium ions are present rather than one, and Na_2CO_3 is not volatile. NaNO_3 may function as a catalyst. However, no emission was observed with NaNO_3 which may have to be volatized in order to be functional as a catalyst. Of all the alkali nitrates, NaNO_3 is the least volatile [40].

Alternatively, based on the previously observed emission from NaNO_3 [7], the presence of a field of about 10 V/cm may be required in order for a plasma to form since the mismatch between 217.8164 and 8×27.2 eV is 0.22 eV. In the anomalous discharge of hydrogen due to the presence of NaNO_3 , the weak field may adjust the energy of ionizing Na^+ to Na^{4+} to match the energy of 8×27.2 eV to permit a novel reaction of atomic hydrogen.

Another possible explanation for the field dependence of the emission of NaNO_3 versus RbNO_3 is that the counter ion of the former influences the vacuum ionization energies to a significant extent. Thus, the counter ion may more substantially alter the enthalpy of the triple ionization reaction of Na^+ to Na^{4+} , especially given the large enthalpy of this reaction.

5. Conclusions

A plasma of hydrogen and certain alkali ions was generated as recorded via EUV spectroscopy and hydrogen Balmer and alkali line emissions in the visible range. The plasma formed at low temperatures (e.g. $\approx 10^3$ K) from atomic hydrogen and a catalyst comprising one of potassium, rubidium, cesium, and their carbonates and nitrates. These atoms and ions ionize to provide a catalyst with a net enthalpy of reaction of an integer multiple of the potential energy of atomic hydrogen ($m \times 27.2$ eV $m = \text{integer}$) to within 0.1 eV, and comprise only a single ionization in the case of a potassium or rubidium ion. Whereas, the chemically similar atoms of sodium and sodium and lithium carbonates and nitrates which do not ionize with these constraints caused no emission. EUV radiation from hydrogen and alkali lines emitted by the cell loaded with catalyst and operated in hydrogen requires a minimum temperature and

atomic hydrogen produced by dissociation of molecular hydrogen by the hot filament. The heat from the filament and possibly the weak dipole field from the filament may sustain the hydrogen plasma, but it is not essential because in some cases, hydrogen lines or alkali lines were emitted during times when this voltage was set to zero. An anomalous afterglow duration of about 1–2 s was recorded in the case of potassium, rubidium, cesium, K_2CO_3 , RbNO_3 , and CsNO_3 . These atoms and ions ionize to provide a catalyst with a net enthalpy of reaction of an integer multiple of the potential energy of atomic hydrogen to within less than the thermal energies at $\approx 10^3$ K and involve only a single ionization in the case of a potassium or rubidium ion. An electric field of about 10 V/cm may be required in order for NaNO_3 to be catalytic. No unusual behavior was observed with the each control noncatalyst.

The release of energy from hydrogen was evidenced by the hydrogen Lyman and Balmer emission and alkali line emission which identifies the presence of a plasma. The persistence of emission following the removal of all of the power to the cell indicates that novel chemical power source is present.

Reports of the formation of novel compounds provide substantial evidence supporting a novel reaction of hydrogen as the mechanism of the observed EUV emission, anomalous discharge, and anomalous afterglow duration. Novel hydrogen compounds have been isolated as products of the reaction of atomic hydrogen with atoms and ions identified as catalysts in the reported EUV studies [6–31]. Novel inorganic alkali and alkaline earth hydrides of the formula MH^+ and MH^*X wherein M is the metal, X, is a singly negatively charged anion, and H^* comprises a novel high binding energy hydride ion were synthesized in a high temperature gas cell by reaction of atomic hydrogen with a catalyst such as potassium metal and MH , MX or MX_2 corresponding to an alkali metal or alkaline earth metal compound, respectively [18,21,31]. Novel hydride compounds were identified by (1) time of flight secondary ion mass spectroscopy which showed a dominate hydride ion in the negative ion spectrum, (2) X-ray photoelectron spectroscopy which showed novel hydride peaks and significant shifts of the core levels of the primary elements bound to the novel hydride ions, (3) proton nuclear magnetic resonance spectroscopy (NMR) which showed extraordinary upfield chemical shifts compared to the NMR of the corresponding ordinary hydrides, and (4) thermal decomposition with analysis by gas chromatography, and mass spectroscopy which identified the compounds as hydrides. The implications are that a vast new energy source and a new field of hydrogen chemistry have been discovered.

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